

UNCLASSIFIED

AD NUMBER	
AD319681	
CLASSIFICATION CHANGES	
TO:	UNCLASSIFIED
FROM:	CONFIDENTIAL
LIMITATION CHANGES	
TO: Approved for public release; distribution is unlimited.	
FROM: Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 07 OCT 1960. Other requests shall be referred to Ordnance Coros, Department of the Army, Washington, DC 20310.	
AUTHORITY	
31 Oct 1972, DoDD 5200.10; ORD D/A per form 55	

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD _____

*Reproduced
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS
DOD DIR 5200.10

UNCLASSIFIED

CONFIDENTIAL

AD

319 681

*Reproduced
by the*

**ARML. SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA**



CONFIDENTIAL

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

CONFIDENTIAL

Report No. P-60-12

Part I
Metallo-Organic

Quarterly

Copy No. 63

October 7, 1960

ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION

HUNTSVILLE, ALABAMA



REPORT NO. P-60-12

**QUARTERLY PROGRESS REPORT
ON SYNTHETIC CHEMISTRY (U)**

Part I

Metallo-Organic Chemistry

April 1-June 30, 1960

ORDNANCE CORPS, DEPARTMENT OF THE ARMY

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U. S. C., Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

REGRAIDING DATA CANNOT BE PREDETERMINED

CONFIDENTIAL

AS AD NO. 319 681

XEROX

ASTIA
16
A

ERRATA

1. Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-59-18, Part I, Metallo-Organic Chemistry, December 28, 1959.

Figure 13 on page 24 should read,

B^{11} NMR Spectrum of $Et_2NH-B_2H_5$

2. Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-60-6, Part I, Metallo-Organic Chemistry, July 8, 1960.

• Figures 9 and 10 on page 16 should be interchanged.

CONFIDENTIAL

ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

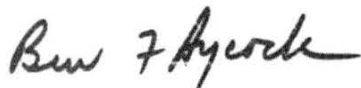
REPORT NO. P-60-12

QUARTERLY PROGRESS REPORT ON SYNTHETIC CHEMISTRY (U)

Part I

Metallo-Organic Chemistry

Approved:



Ben F. Aycock
Head, Synthetic Chemistry
Section



Allen R. Deschere
General Manager

Contributing Staff:

Metallo-Organic Chemistry

John A. Dupont
Bruce M. Graybill
John J. Miller
Anthony R. Pitochelli
Robert A. Wiesboeck

M. Frederick Hawthorne
Group Leader

Analytical Chemistry

Earl D. Bosserman
Carolyn P. Haney
R. Donald Strahm

Keith A. Booman
Group Leader

October 7, 1960
(Written September 2, 1960)

Work reported herein was carried
out under the following contract.

DA-01-021 ORD-11878

CONFIDENTIAL

CONFIDENTIAL

FOREWORD

This report is one in a series of Quarterly Progress Reports issued by the Redstone Arsenal Research Division of the Rohm & Haas Company. The complete list of reports, together with approximate issuance dates, is shown below:

<u>Synthetic Chemistry</u> *	<u>Propellant Chemistry</u>	<u>Physical Chemistry</u>	<u>Engineering Research</u>	<u>Interior Ballistics</u>	<u>Solid Propellant Processing</u>
Jan. 25	Feb. 25	Mar. 25	Jan. 10	Feb. 10	Mar. 10
Apr. 25	May 25	Jun. 25	Apr. 10	May 10	Jun. 10
<u>Jul. 25</u>	Aug. 25	Sept. 25	Jul. 10	Aug. 10	Sept. 10
Oct. 25	Nov. 25	Dec. 25	Oct. 10	Nov. 10	Dec. 10

The distribution of all reports is made according to the JANAF Mailing List plus approved supplements.

Research on two contracts, DA-01-021 ORD-784 and DA-01-021 ORD-785, supported by Air Force funds, is reported in a separate series of quarterlies published on March 25, June 25, September 25 and December 25.

* Includes sections on Metallo-Organic and Organic Chemistry.

CONFIDENTIAL

C O N F I D E N T I A L

ROHM & HAAS COMPANY

REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

ABSTRACT

Preparation of the new boron hydride, tentatively identified as octadecaborane-22, has been investigated. A new tetramethylammonium salt, apparently that of $[B_8H_8]^-$, has been isolated from the reaction of ferric ion with triethylammonium perhydrodecaborate.

Optical resolution of a nonacborane has been accomplished.

The kinetic study of nonacborane formation was completed and second order rate constants for a variety of carboranes are given. Deuterated carboranes did not exhibit a kinetic isotope effect. A Hammett treatment of the reaction indicates moderate sensitivity to substituents.

Electrophilic exchange of carborane with deuterium chloride, which occurs at a faster rate than that with decaborane, allows the entrance of only four deuterium atoms. Present evidence suggests that the 6 and 9 positions are affected along with either the 1 and 3 or 2 and 4 positions.

Pyrolysis of hydrazine *t*-butylborane provided a material of empirical composition $C_4H_{11}BN_2$, which has been studied chemically in an effort to elucidate the structure.

Efforts to synthesize a B-N carborane have been futile but are continuing.

A mechanism for the formation of $B_{10}H_{12}(Et_2S)_2$ is postulated

C O N F I D E N T I A L

CONFIDENTIAL

ABSTRACT (Continued)

on the basis of kinetic studies of this reaction. Preliminary data for the triphenylphosphine-decaborane reaction have also been obtained.

N-Alkyldecaboranes have been prepared by a new scheme which is suitable for synthesis of unsymmetrical $B_{10}H_{12}X_2$ derivatives. A number of these materials are described.

Methanolysis of tetramethylammonium nonaborane has provided tetramethylammonium triborane, $(CH_3)_4NB_3H_9$; the structure was confirmed by comparison with an authentic sample.

CONFIDENTIAL

TABLE OF CONTENTS

DISCUSSION	Page
I. OCTADECABORANE-22	1
A. Preparation	1
B. Properties	4
C. The Reaction of $(Et_3NH)_2B_{10}H_{10}$ with Ferric Ion, another Triethylammonium Salt	4
II. DICARBOUNDECABORANE-13 CHEMISTRY	5
A. The Resolution of a Nonacaborane	5
B. Kinetics of the Formation of Nonacaboranes	6
III. CARBORANE CHEMISTRY	8
A. The Electrophilic Exchange of Deuterium Chloride with Carborane	8
IV. REACTIONS OF $RBH_2 \cdot NR_3$ WITH HYDRAZINE	13
V. ATTEMPTED PREPARATION OF B-N CARBORANES	16
VI. AROMATIC ORGANOBORANES	17
VII. REACTIONS OF DECABORANE	17
A. The Kinetics and Mechanism of $B_{10}H_{12}(Et_2S)_2$ Formation	17
B. Reactions of Phosphines with Decaborane	22
C. New Synthesis of N-Alkyl "Dekazenes" and Unsymmetrical $B_{10}H_{12}$ Derivatives	23
VIII. PREPARATION OF TETRAMETHYLAMMONIUM TRIBORANE FROM TETRAMETHYLAMMONIUM NONABORANE	26

TABLE OF CONTENTS

(Continued)

EXPERIMENTAL	Page
I. OCTADECABORANE-22	28
A. Preparation of Octadecaborane-22	28
C. The Reaction of $(Et_3NH)_2B_{18}H_{18}$ with Ferric Ion, another Triethylammonium Salt	29
II. DICARBONDECABORANE-13 CHEMISTRY	29
A. Resolution of a Nonacborane	29
C. Kinetics of the Formation of Nonacborane	31
III. CARBORANE CHEMISTRY	32
A. Electrophilic Exchange of Deuterium Chloride with Carborane	32
IV. REACTIONS OF $RBH_2 \cdot N(CH_3)_3$ WITH HYDRAZINE	33
VI. AROMATIC ORGANOBORANES	35
VII. REACTIONS OF DECABORANE	35
C. New Synthesis of N-alkyl "Dekazenes" and Unsymmetrical $B_{10}H_{12}$ Derivatives	37
VIII. PREPARATION OF TETRAMETHYLAMMONIUM TRIBORANE FROM TETRAMETHYLAMMONIUM NONABORANE	39

CONFIDENTIAL

DISCUSSION

I. OCTADECABORANE -22

A. Preparation

The isolation of a new higher boron hydride, octadecaborane ($B_{18}H_{22}$), was reported previously¹. The isolation of a B_{18} hydride from a system in which a B_{10} hydride is the precursor demands a coupling reaction somewhere in the reaction sequence. Two mechanisms are possible: in the first, coupling to a B_{20} species could occur with subsequent loss of two borons to form the stable B_{18} hydride. On the other hand, loss of a boron atom from a B_{10} species could generate a reactive B_9 species which might then couple to form the higher hydride.

The first opportunity for coupling occurs in the reaction of triethylamine with decaborane, leading to the formation of the perhydrodecaborate anion. A cryoscopic determination of the apparent molecular weight of triethylammonium perhydrodecaborate in aqueous solution gave a value of 107 mass units on extrapolation to infinite dilution. The observed values for the formula weights for a 2:1 and 4:1 electrolyte are 321 and 535, respectively. The theoretical values for these species are 322.2 and 644.4. It thus appears that triethylammonium perhydrodecaborate (I) contains a $B_{10}H_{10}^{-2}$ anion, and coupling occurs after this step.

Oxidative coupling resulting from the reaction of I with ferric ion is a definite possibility. Microanalysis indicated that the composition of the major product of this reaction very closely approached $(Et_3NHB_{10}H_{10})_n$ (II). Since an anion of this composition and charge would be a free radical, a coupled anion (n even) satisfies the electronic requirements. The determination of the apparent molecular weight of this salt was hindered by the lack of a suitable solvent, but the use of formamide now appears to hold promise. The insolubility of the triethylammonium salt in water prevented the use of this solvent, while use of water-soluble alkali metal salts was frustrated by their tendency

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, No. P-60-6, Part I, Metallo-Organic Chemistry, July 1960.

CONFIDENTIAL

to form hydrates. The determination of the character of this anion is required for an understanding of the mechanism and further work will be carried out.

When an alcoholic solution of II was passed through a column containing the acid for γ of IR-120, no coupling occurred, as demonstrated by the fact that the tetramethylammonium derivatives of unexchanged and exchanged II had identical infrared spectra (Fig. 1).

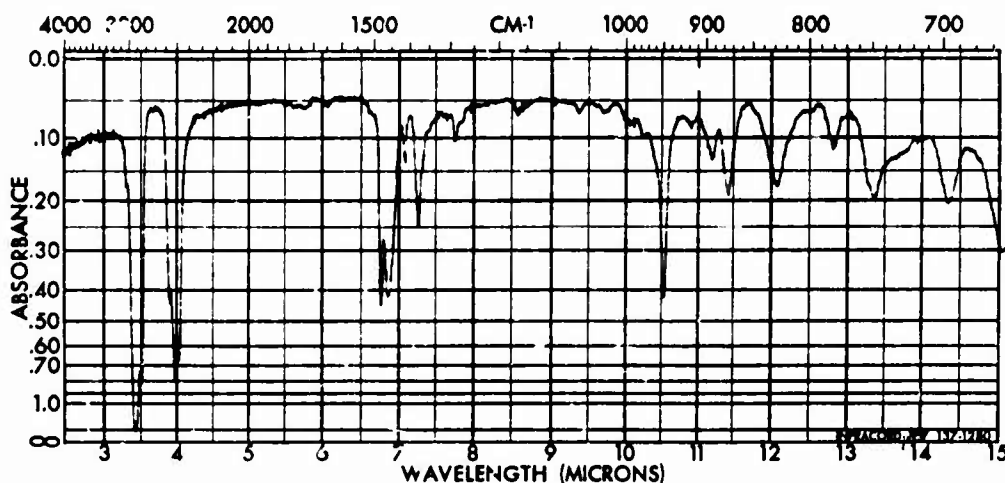


Fig. 1 Infrared spectrum of $(\text{CH}_3)_4\text{N}(\text{B}_{10}\text{H}_{10})$

The next step in the synthesis, evaporation of the ethanolic eluant, resulted in the formation of a viscous yellow semi-solid. Addition of water to an ether solution of this semi-solid caused gassing and the ether layer became quite yellow. Evaporation of the ether left crude $\text{B}_{10}\text{H}_{22}$. The same gassing was observed when the yellow material was added to 95% ethanol. Addition of aqueous tetramethylammonium chloride to the yellow alcoholic solution caused precipitation of $(\text{CH}_3)_4\text{NB}_{10}\text{H}_{21}$, identified by comparison of its infrared spectrum to that of authentic $(\text{CH}_3)_4\text{NB}_{10}\text{H}_{21}$ (Fig. 2) which was prepared by the

reaction of aqueous $(\text{CH}_3)_4\text{NCl}$ with ethanolic $\text{B}_{12}\text{H}_{22}$. It seems reasonable to conclude that it is during this step that two boron atoms are removed from a B_{20} ion.

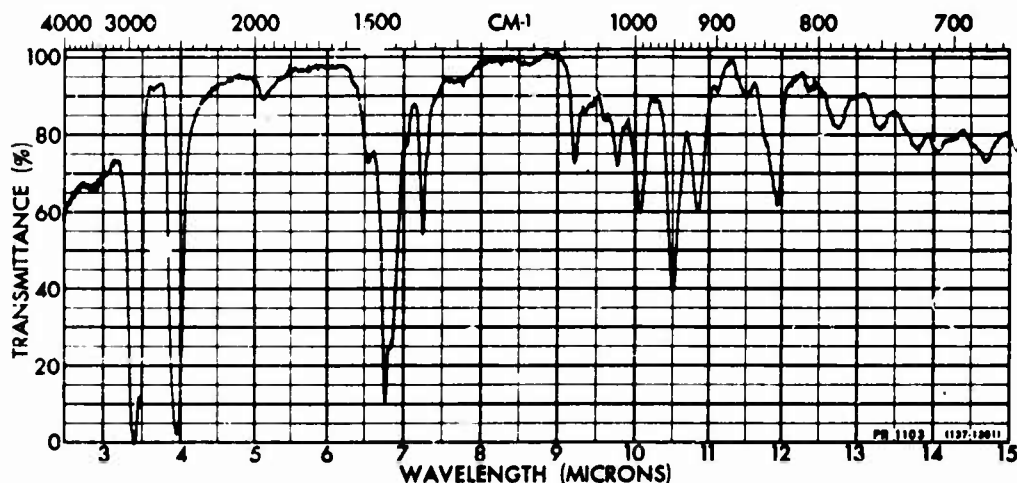


Fig. 2 Infrared spectrum of $(\text{CH}_3)_4\text{N}(\text{B}_{10}\text{H}_{21})$

The role alcohol plays in the conversion is not presently understood. Merely refluxing unexchanged or ion-exchanged II in ethanol has no effect. In the first case, starting material is recovered, while in the second case evaporation of refluxed exchanged solution gives the same oil as evaporated unrefluxed solution; infrared spectra are identical. Further, acidification of II in ethanol with dry HCl , or aqueous HBF_4 with subsequent concentration does not produce hydride; II is recovered. It is interesting to note that each successful conversion of II to $\text{B}_{10}\text{H}_{22}$ involves three points: (1) exchange of II in alcoholic solution, (2) reduction of the solution to a low volume either by evacuation or thermal evaporation, and (3) addition of water either during or after evaporation.

B. Properties

Octadecaborane did not appear to be as reactive as decaborane. It survived prolonged refluxing in acetonitrile. On the other hand, it appeared to react with triphenylphosphine, but the derivative has not been characterized.

Ultraviolet spectra of octadecaborane in cyclohexane and acetonitrile were obtained and found to differ, as expected from visual observations of the solutions. The purple-blue fluorescent solution in cyclohexane showed two maxima; λ_{max} , 272 m μ , ϵ_{max} , 4250; λ_{max} , 331 m μ , ϵ_{max} , 720. The yellow acetonitrile solution had one absorption not found in the spectrum of the undissociated hydride and two shoulders that might be attributed to this species. The maxima observed in this solvent were at 378 m μ , ϵ_{max} , 5250, a shoulder at about 330, ϵ_{max} 4080, and a very poorly defined shoulder at about 265 m μ . Acetonitrile is apparently sufficiently basic to cause some ionization.

C. The Reaction of $(\text{Et}_3\text{NH})_2\text{B}_{10}\text{H}_{10}$ with Ferric Ion, another Triethylammonium Salt

The reaction described earlier¹ between $(\text{Et}_3\text{NH})_2\text{B}_{10}\text{H}_{10}$ and Fe^{+3} may be made to yield a different product by allowing the substances to interact at higher concentration. The new salt appeared to have the composition, $(\text{Et}_3\text{NHB}_9\text{H}_9)_n$ (III). III differs from II in its solubility in ethanol and was first observed as an ethanol-insoluble fraction present in preparations of II which were run at higher concentrations. The new salt could be recrystallized from acetonitrile and ethanol, m. 202-203° d. The infrared spectrum of III (Fig. 3) was superficially similar to II but had an absorption at 1870 cm^{-1} which was not present in II, allowing easy recognition. This absorption, which survived recrystallization, appeared to be characteristic of the molecule, but present information allowed no assignment.

The reactions of this species will be pursued.

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, No. P-60-6, Part I, Metallo-Organic Chemistry, July 1960.

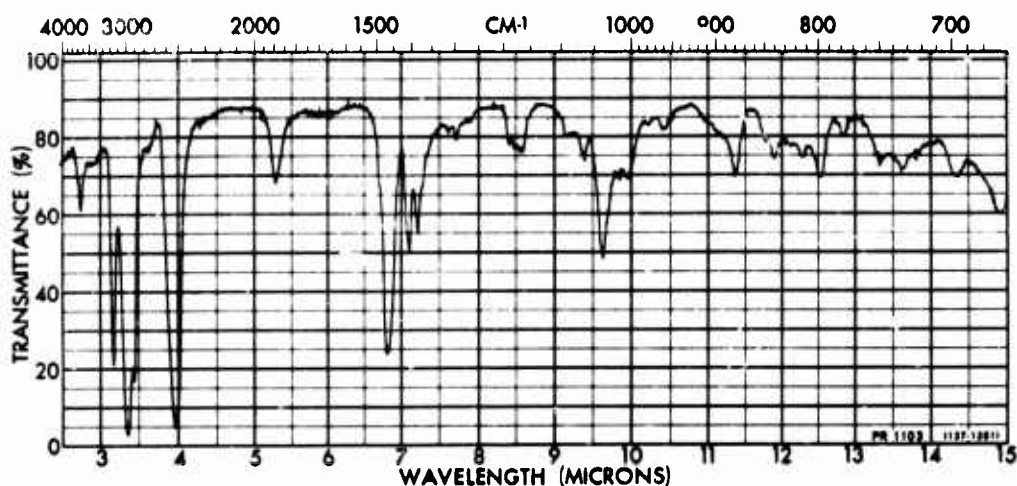


Fig. 3 Infrared spectrum of $(\text{Et}_3\text{NH B}_8\text{H}_8)_n$

II. DICARBOUNDECABORANE- ^{13}C CHEMISTRY

A. The Resolution of a Nonacborane

Nonacborane, formed from carborane by removal of one boron atom from the icosahedron, should be capable of existing in enantiomeric forms if properly substituted. After several attempts to resolve the brucine salt of phenylnonacborane failed, it was suspected that racemization might have taken place by migration of the substituent. Thus 11-methyl-12-phenylnonacborane-brucine was successfully resolved by fractional crystallization from acetonitrile. In this case fractions with a molar rotation from -17.4° to $+13.0^\circ$ were obtained. The least soluble diastereomer ($\alpha_{\text{molar}} = -17.4^\circ$) was converted to the tetramethylammonium salt by refluxing it in 30% ethanolic potassium hydroxide followed by the addition of tetramethylammonium ions to the diluted aqueous solution. The precipitated salt exhibited a molar rotation of -16.8° . When this salt was run through the acid form of an

¹ Nonacborane will be used as an abbreviation of dicarboundecaborane.

ion exchange resin (Amberlite IR 120) in methanol, the optically active free nonacarborane was obtained (molar rotation -14.8°). There was no indication of racemization. Identical treatment of the other diastereomer produced a tetramethylammonium salt with a molar rotation of $+16.6^\circ$. The corresponding free nonacarborane possessed $\alpha_{\text{molar}} = +15.0^\circ$. The existence of isomers strongly supports the proposed structure for carborane and nonacarboranes. Furthermore, the apparent racemization of mono-substituted nonacarboranes suggests that a phenyl group can migrate easily between the carbon atoms. Racemization by means other than migration seems unlikely since the free 11-methyl-12-phenylnonacarborane does not racemize.

B. Kinetics of the Formation of Nonacarboranes

Kinetic studies of the formation of nonacarboranes were essentially completed. Comparison of the rates of formation of mono- and disubstituted nonacarboranes showed a steric deceleration when the second substituent was introduced. These results are shown in Table I.

Table I

SECOND ORDER RATE CONSTANTS AT 75° IN 50% AQUEOUS ETHANOL

	<u>$k \times 10^4 \text{ [l} \cdot \text{mole}^{-1} \cdot \text{sec.}^{-1}]$</u>
Nonacarborane	$1.48 \pm .03$
Methylnonacarborane	$1.42 \pm .03$
Dimethylnonacarborane	$0.79 \pm .02$
Phenylnonacarborane	$7.30 \pm .14$
Diphenylnonacarborane	$1.13 \pm .09$

Isotopic labeling of carboranes with deuterium in the 1, 2, 3, 4 position produced essentially no deuterium in the degradation reaction. 1, 2, 3, 4-Tetradeuterophenylcarborane liberated 97% H_2 and only 3% HD. 1, 2, 3, 4-Tetradeutercarborane formed 10-12% HD which might be partly due to deuteration in other positions. In no case was a kinetic isotope effect observed with deuterated carboranes.

This supports a degradation process in which the base attacks a boron atom next to a carbon atom; in other words one of the 5, 7, 8, 10 or 6, 9 boron atoms is removed. Since position isomers are never observed the 6, 9 boron atoms are prime candidates.

A Hammett treatment of the degradation reaction was carried out with several phenyl substituted phenylcarboranes. Most of the compounds were prepared from phenylcarborane. Nitration yielded m- and p-nitro-phenylcarboranes (m.p. 122° and 168°) which were separated by fractional crystallization from methylene chloride / cyclohexane. The isomers were reduced to the amines, diazotized, and reacted with the appropriate agent. The identity of the nitro isomers was shown by oxidation to the corresponding nitrobenzoic acids in aqueous alkaline potassium permanganate solution. The less soluble, higher melting isomer yielded p-nitrobenzoic acid (m.p. 242°). All kinetic runs were carried out in 50% aqueous ethanol at 75°, as described earlier.¹ A rho value of + 1.32 was obtained, indicating that the reaction is moderately sensitive to substituents which change the electron density at the reaction site.

The second-order rate constants of phenyl-substituted phenyl-carboranes were obtained and are shown in Table II.

Table II

<u>Substituent</u>	<u>$k \times 10^3 [l \cdot mole^{-1} \cdot sec.^{-1}]$</u>
-H	.730 \pm .014
<u>p</u> -F	1.02 \pm .02
<u>m</u> -F	1.49 \pm .02
<u>p</u> -Br	1.29 \pm .02
<u>m</u> -Br	1.70 \pm .02
<u>p</u> -NO ₂	3.92 \pm .05
<u>m</u> -NO ₂	3.73 \pm .04
<u>p</u> -NH ₂	.239 \pm .002
<u>m</u> -NH ₂	.496 \pm .007

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, No. P-60-6, Part I, Metallo-Organic Chemistry, July 1960.

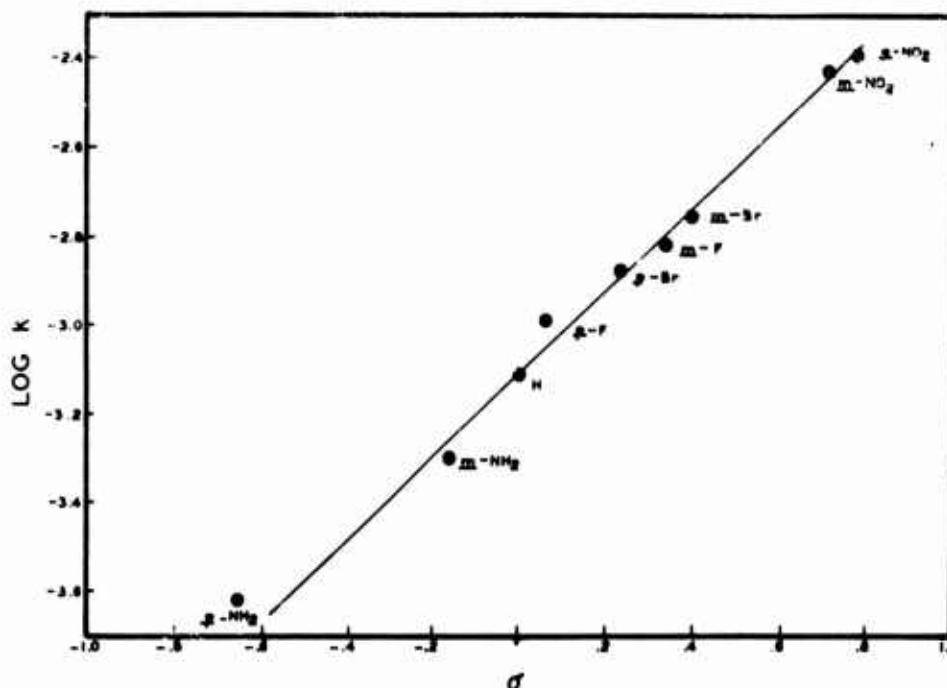


Fig. 4 Log k as a function of σ .

It was noticed that nearly all of the carboranes developed impurities on standing in closed bottles under nitrogen at ambient temperature. These impurities would degrade considerably faster than the pure carborane and rates of reaction of samples older than two days increased as much as ten percent. This was most surprising since carboranes are very stable toward oxidizing agents such as potassium permanganate.

III. CARBORANE CHEMISTRY

A. The Electrophilic Exchange of Deuterium Chloride with Carborane

The electrophilic exchange of deuterium chloride with carborane and aluminum chloride catalyst was carried out. Essentially the same

experimental techniques were employed as were used in the previously reported¹ electrophilic exchange of decaborane. The course of exchange was monitored by withdrawing samples at regular intervals and recording the B¹¹ n.m.r. spectrum. Determination of the deuterium content of the resulting samples was not carried out. However, in lieu of precise quantitative data, these qualitative results led to some reasonable conclusions.

A series of B¹¹ n.m.r. spectra showing the progressive spectral changes as a function of reaction time is shown in Fig. 5. The relatively rapid change in the spectra with time, compared to that previously observed in the case of decaborane indicates qualitatively that the deuterium exchange of carborane occurs at a significantly faster rate. This corroborates the observation of Callery Chemical Company that the B-alkylation of carborane proceeds much faster than that of decaborane. It is apparent upon examination of the successive spectra that the two lowest field-doublets, a and b (shown in Fig. 6), each representing two equivalent boron atoms, are undergoing exchange. This is shown by the disappearance of the discernible member of each of the doublets. No observable changes in the spectra occurred after approximately seven hours reaction time, indicating a cessation of exchange after four deuterium atoms were introduced. Measurement of the area of the high field peak (the high field member of two coincidental doublets, c and d, representing sets of two and four boron atoms) yielded a value equivalent to six boron atoms, thereby providing additional supporting evidence for the fact that only four borons are involved in exchange. It can be seen by comparison of the B-H versus B-D absorptions in the infrared spectrum (Fig. 7) of the final product of the exchange that the areas are in rough agreement with the above conclusions. It is of significance that no carbon substitution has occurred since no C-D stretching band is observed.

In hopes of partially resolving the various resonance lines in the B¹¹ spectrum of carborane a sample of deuterium labeled carborane was prepared. This was accomplished by the reaction of 1,2,3,4-

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, Part I, Metallo-Organic Chemistry, No. P-60-6, July 1960.

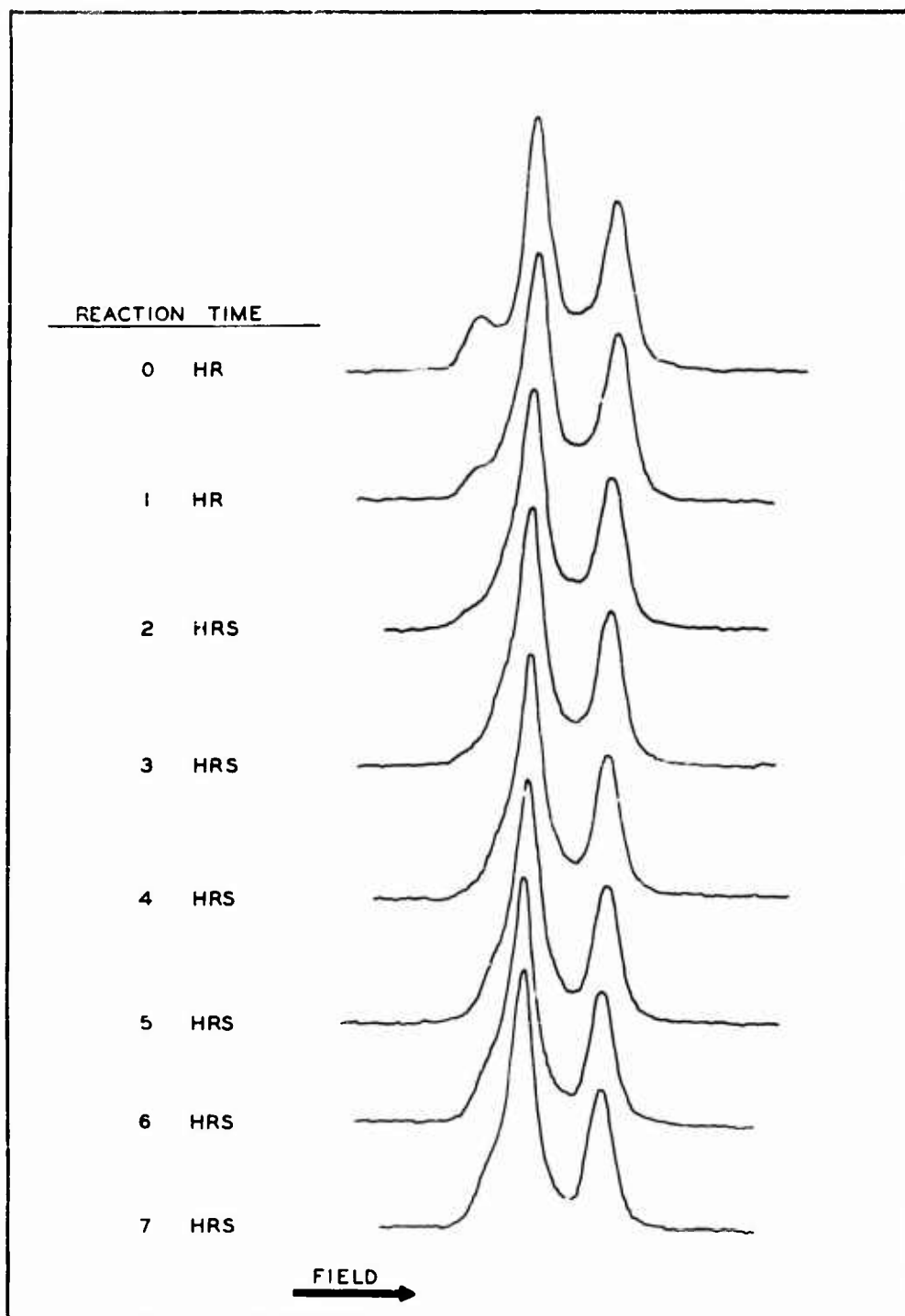


Fig. 5 Series of B'' n.m.r. spectra showing the progressive spectral changes as a function of reaction time.

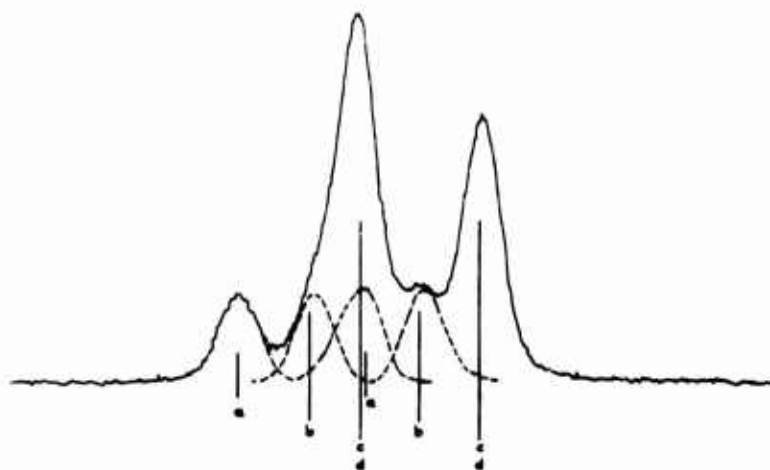


Fig. 6 B¹¹ n.m.r. spectrum of carborane.

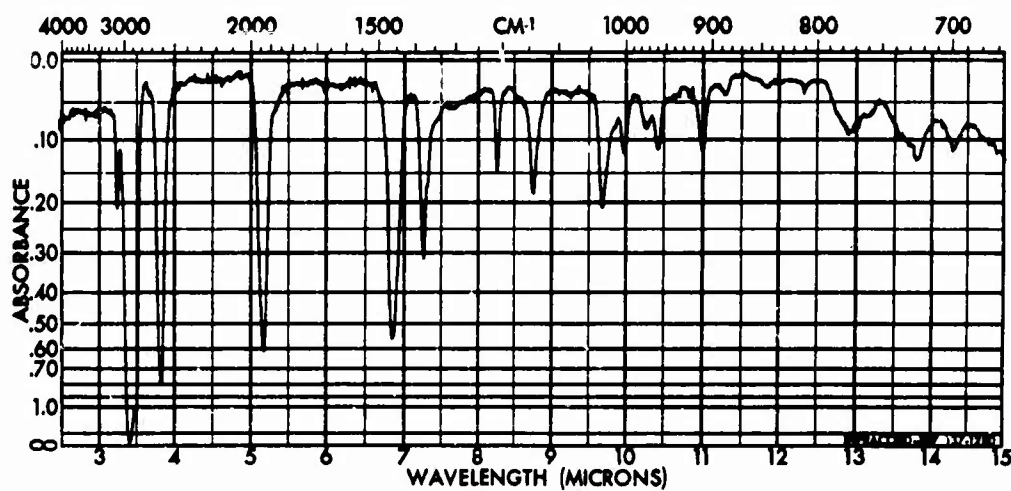


Fig. 7 Infrared spectrum of B-deuterated carborane.

deuterium labeled bis-acetonitrilo-decaborane (prepared from decaborane containing an average of 3.7 deuterium atoms per mole) with acetylene in acetonitrile solvent. The yield amounted to twenty-five percent based on BAND. The B^{11} n.m.r spectrum of this material, shown in Fig. 8, indicated that the lowest field doublet (a) collapsed. Also, the doublet, d, which is coincident with the 5, 7, 8 and 10 doublet appeared to have collapsed. Due to the fact that the original decaborane used in the preparation of the carborane sample was not fully deuterated in the 1, 2, 3 and 4 positions total collapse of the representative doublets was not effected. This reduced the certainty of identification. Another element of uncertainty which must be considered is the possibility of deuterium migration. However on the basis of the spectrum on hand it can be concluded that the 1, 3 and 2, 4 borons are represented by the lowest field doublet and that doublet which is coincident with the 5, 7, 8, and 10 doublet. If this assignment is employed it follows that two of the four boron atoms involved in the electrophilic exchange are those in the 6 and 9 positions. The remaining two equivalent positions are either the 1, 3 or 2, 4 boron atoms. No conclusion as to which of these pairs is involved in the exchange can be made.

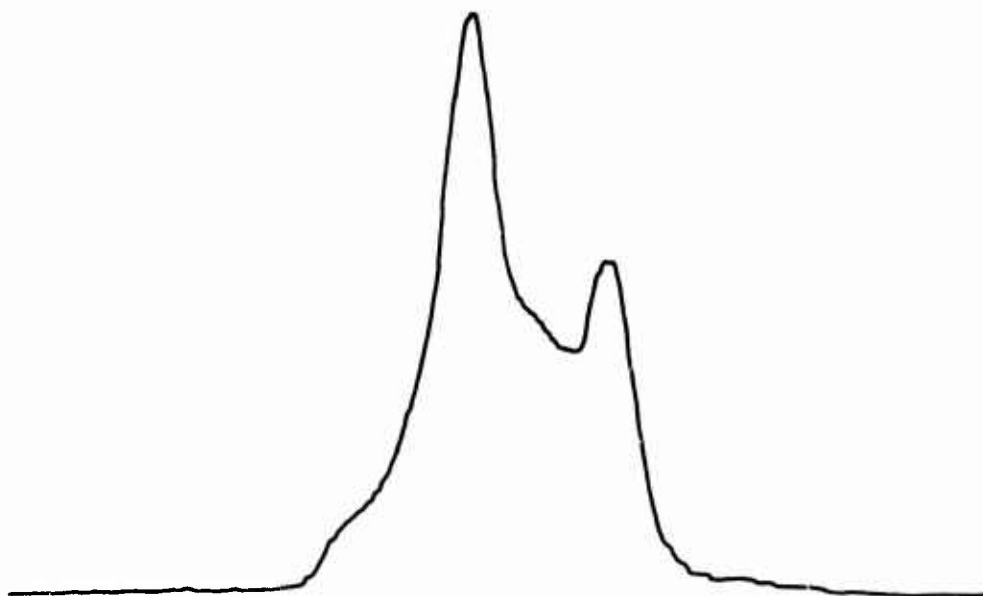
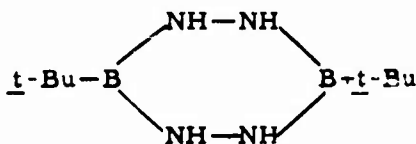


Fig. 8 B^{11} n.m.r. spectrum of 1, 2, 3, 4 - deuterated carborane.

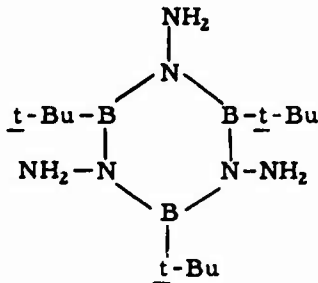
IV. REACTIONS OF $\text{RBH}_2 \cdot \text{NR}_3$ WITH HYDRAZINE

The reaction of trimethylamine t-butylborane with hydrazine to give hydrazine t-butylborane was described in the last quarterly report¹. As reported, one attempted preparation of hydrazine t-butyl borane led to the isolation of a small amount of another material which was assigned the structure (I). Attempts to repeat this preparation were



I

futile, although the same material was obtained by pyrolysis of hydrazine t-butylborane at 140° . This type of reaction might be expected to give a borazole. Elemental analysis was consistent with the empirical formula $\text{C}_4\text{H}_{11}\text{BN}_2$, which fit both structure I and tri-B-t-butyl tri-N-amino borazole (II).



II

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, Part I, Metallo-Organic Chemistry, No. P-60-6, July 1960.

The infrared spectrum, given previously¹, appeared to have only a single N-H stretching absorption and no N-H deformation, which probably should appear in the aminoborazole. The proton nuclear magnetic resonance spectrum (Fig. 9) indicated, however, that there are two types of N-H present in the molecule.

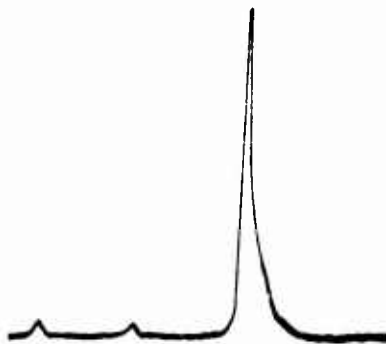


Fig. 9 H^1 n.m.r. spectrum of compound obtained from the pyrolysis of hydrazine t-butylborane.

Deuteration of this material can be accomplished by stirring an ethereal solution with deuterium oxide. Not all of the N-H, as evidenced by the infrared spectrum, is deuterated. The proton n.m.r. spectrum shows that the low field peak is apparently the only one affected.

Acetylation of the pyrolysis product was unsuccessful with acetyl chloride, but when acetic anhydride was employed both as solvent and reactant, the reaction followed the desired course. The acetylated product (IR spectrum Fig. 10) apparently contains two types of carbonyl groups and no longer exhibits N-H stretching vibrations. Appearance of a hydroxyl band in the spectra of samples stored for a short while indicated that air oxidation occurs. Removal of these hydroxyl containing impurities was accomplished by washing the material with water. Analytical data suggested that two acetyl groups were added to the substrate and one nitrogen atom removed. No structure has been postulated for this material. Reduction of this product with lithium aluminum hydride was unsuccessful.

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, Part I, Metallo-Organic Chemistry, P-60-6, July 1960, p. 46.

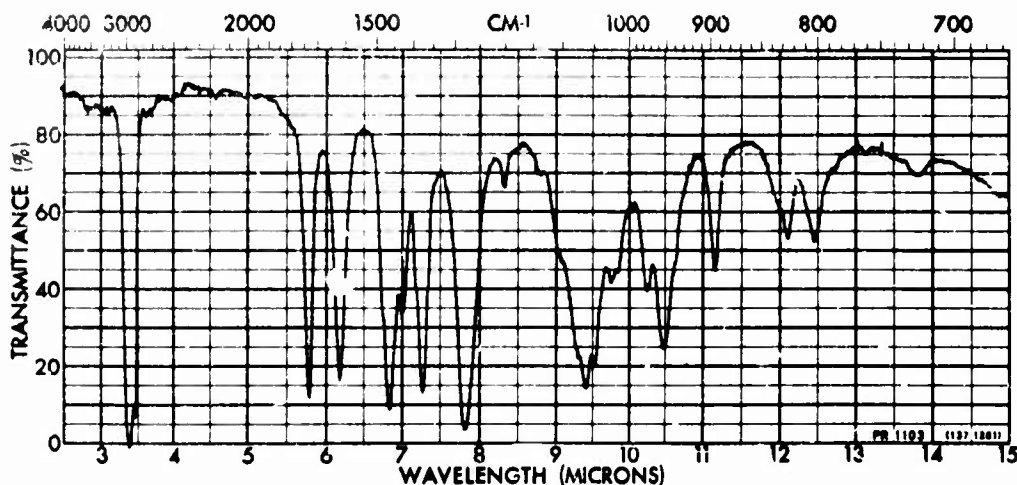


Fig. 10 Infrared spectrum of compound obtained upon acetylation of pyrolysis product.

Reaction of the pyrolysis product with iodine provided a variety of products. A red-brown solid was isolated from the reaction; this material was decolorized when it was stirred with 10% sodium thiosulfate and a light yellow solid, m.p. $132-133^{\circ}$, which was insoluble in ether and water, was isolated. Treatment of this material with ethanol provided a white solid, m.p. $134-135^{\circ}$, which was apparently different from the light yellow material. Analysis is in progress. The infrared spectrum of the product is shown in Fig. 11.

The usefulness of alkylamine organoboranes as intermediates led to attempts to prepare a polymerizable amine borane. Synthesis of trimethylamine vinylborane was attempted. Vinyl dibutylboronate¹ was prepared by treatment of methyl borate with vinylmagnesium chloride and then with *n*-butanol. Reduction of this ester with lithium aluminum hydride in the presence of trimethylamine did not provide the desired product. It appeared that the double bond was reduced and the product isolated was trimethylamine ethylborane. There was no indication of unsaturation in the materials isolated from the reaction.

¹ D. S. Matteson, J. Am. Chem. Soc., 81, 5004 (1959); private communication.

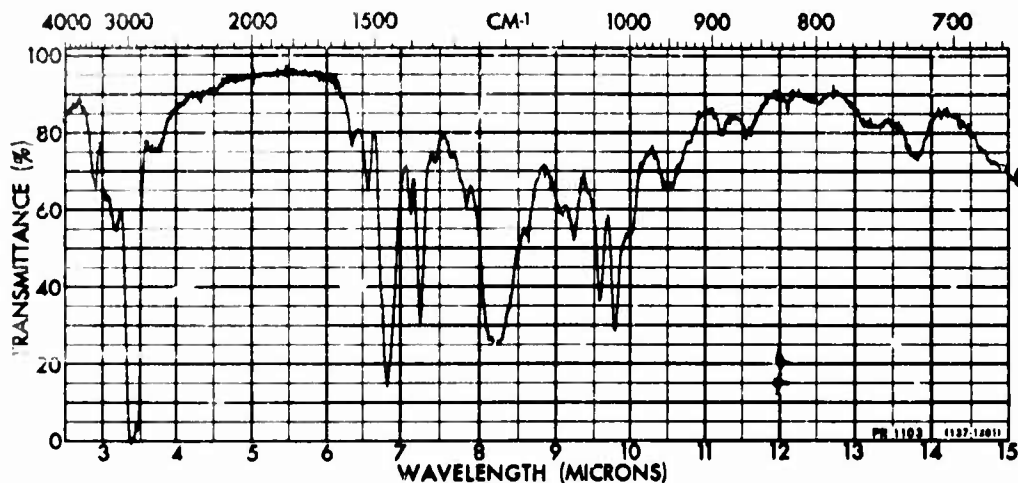


Fig. 11 Infrared spectrum of product obtained upon reaction of the pyrolysis product with iodine.

V. ATTEMPTED PREPARATION OF B-N CARBORANES

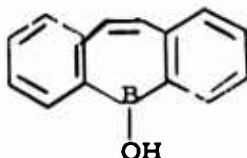
Nitrilium salts are isoelectronic with acetylenes and thus might possibly lead to carborane type materials containing a nitrogen atom in the icosahedron.

Adducts of boron trichloride and boron trifluoride with acetonitrile were prepared and were used in reactions with bis-acetonitrile decaborane and with bis-ethylsulfide decaborane. No reactions occurred between these materials under a variety of conditions.

N-Ethyl acetonitrilium fluoroborate was synthesized from acetonitrile and triethyl oxonium fluoroborate and treated with bis-ethylsulfide decaborane; results were not promising but work on the reaction is being continued.

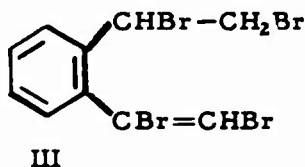
VI. AROMATIC ORGANOBORANES

The synthesis of the following material was reported recently¹.



The product was isolated as its ethanolamine adduct and as such is probably not truly aromatic. Synthesis according to the scheme proposed in the last quarterly² is again in progress. A method for the preparation of o-diethynylbenzene has been obtained; this employs potassium t-butoxide³ to dehydrohalogenate o-bis- (1,2-dibromoethyl) benzene.

The structure of the bromination product of o-ethynylstyrene has been shown to be III rather than the indane previously proposed.² Proton nuclear magnetic resonance supports this structure.



VII. REACTIONS OF DECABORANE

A. The Kinetics and Mechanism of $B_{10}H_{12}(Et_2S)_2$ Formation

Since the compounds of the type $B_{10}H_{12}X_2$ are such key intermediates in synthetic work, an investigation of the kinetics and mechanism of their formation was initiated. The reaction between ethyl sulfide and decaborane was chosen for study since considerable experience

¹ E. van Tamelen, et. al., Tetrahedron Letters, 14 (1960).

² Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, Part I, Metallo-Organic Chemistry, P-60-6, July 1960.

³ A. S. Hay, J. Org. Chem., 25, 637 (1960).

has been obtained with this reaction and it was known definitely that one mole of hydrogen was evolved during the reaction^{1,2,3}.

The reaction was run at 60.2°C. in toluene solvent and was followed by measuring the pressure of hydrogen evolved. The apparatus consisted of a reaction flask attached to a closed manometer. The flask was completely immersed in the constant temperature bath and slowly agitated by an automatic wrist shaker. When run under pseudo first-order conditions (large excess of ethyl sulfide) the reaction was first order in decaborane. Variation of the ethyl sulfide concentration showed that the reaction was also first order in ethyl sulfide. The reaction rate law with the condition of excess ethyl sulfide⁴ must therefore be,

$$\frac{dH_2}{dt} = k[Et_2S] [B_{10}H_{14}] .$$

The calculated second order rate constants at various concentrations are given in Table III.

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, Part I, Metallo-Organic Chemistry, No. P-59-12, August, 1959.

² *ibid.*, No. P-59-18, December 1959.

³ *ibid.*, No. P-60-6, July 1960.

⁴ The reaction with ethyl sulfide in which excess decaborane is used gives different results. The rate was about five times faster than the normal rate, but four moles of hydrogen were evolved. The solution turned orange as compared to the usual colorless reaction solution. It is apparent that a different reaction occurs in this case. These results are consistent with the proposed mechanism (*vide infra*).

Table III

SECOND ORDER RATE CONSTANTS
IN TOLUENE AT 60.2°C.

Run No.	[B ₁₀ H ₁₄] moles/liter	[Et ₂ S] moles/liter	k ₂ × 10 ⁻³ liters mole-min.
20	0.0595	1.82	1.53
21	0.0595	1.82	1.54
22	0.0598	2.45	1.55
23	0.0598	1.22	1.52
24	0.120	2.45	1.56
32	0.0595	0.61	1.55
33	0.0598	0.61	1.54
34	0.0610	1.215	1.54
44	0.060	2.02	1.59
50	0.059	1.416	1.57
			Avg. 1.55

The rates of reaction and analyses of the evolved gas were also determined for the reaction of ethyl sulfide and various deuterium labeled decaboranes. The results along with gas analyses for the nucleophiles, CH₃CN and Et₂Pφ, are listed in Table IV. All the runs were made in toluene except in the case of acetonitrile which was carried out in pure acetonitrile.

The rate of reaction of ethyl sulfide with bridge and 5,6,7,8,9, and 10 deuterium labeled decaborane was slower than with normal decaborane and the isotope effect was greatest for the reaction with 5,6,7,8,9, and 10 deuterated decaborane as expected. In one of the rate runs some of the unreacted bridge deuterated decaborane was recovered and examined by infrared and n.m.r. spectroscopy. Extensive equilibration of the bridges to the terminal positions had obviously occurred.

Table IV

RESULTS OF THE REACTION OF NUCLEOPHILES
WITH DEUTERATED DECABORANES

Reaction	$k_2 \times 10^{-3}$ at 60.2° C.	$\frac{\text{liter}}{\text{mole-min}}$	k_H/k_D Isotope Effect	Gas Analysis		
				% H ₂	% HD	% D ₂
Et ₂ S + B ₁₀ H _{9.8} D _{4.2} (bridge labeled)	0.84		1.8	53	40	7
Et ₂ S + B ₁₀ H _{3.2} D _{6.8} (labeled bridges and 5, 6, 7, 8, 9, 10 positions)	0.50		3.1	7.6	35.4	57
Et ₂ S + B ₁₀ H _{9.8} D _{4.2} (labeled 1, 2, 3, 4 positions)	1.56		1.0	95	5	0
CH ₃ CN + B ₁₀ H _{9.8} D _{4.2} (bridge labeled)	-		-	43	44	13
Et ₂ Pφ + B ₁₀ H _{9.8} D _{4.2} (bridge labeled)	-		-	30.6	46.6	22.9

This migration of bridge deuterium to the terminal positions was observed to be quite fast in a toluene solution of Et₂S. Equilibration occurred in a matter of minutes at room temperature. The infrared spectrum showed a definite increase of the B-D terminal band as the solution stood in the instrument. Obviously, the gas analysis data can show very little concerning the origin of the evolved hydrogen.

Schaeffer¹ carried out a study of the formation of BAND from bridge deuterio decaborane and came to the conclusion that the hydrogen comes from one bridge and one terminal position. Since in this case equilibration must also occur, doubt is cast on this conclusion.

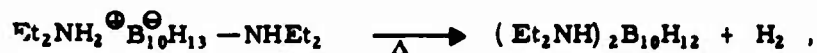
The gas analysis from the reaction of Et₂S and B₁₀H₁₈D₄, labeled in the 1, 2, 3, 4 positions contained no deuterium as expected. A rate run with this same labeled decaborane did not show a secondary kinetic isotope effect and again indicated that the bottom of the decaborane molecule does not enter into or affect the reaction.

¹ R. Schaeffer, WADC Technical Note 59-258, July 1959.

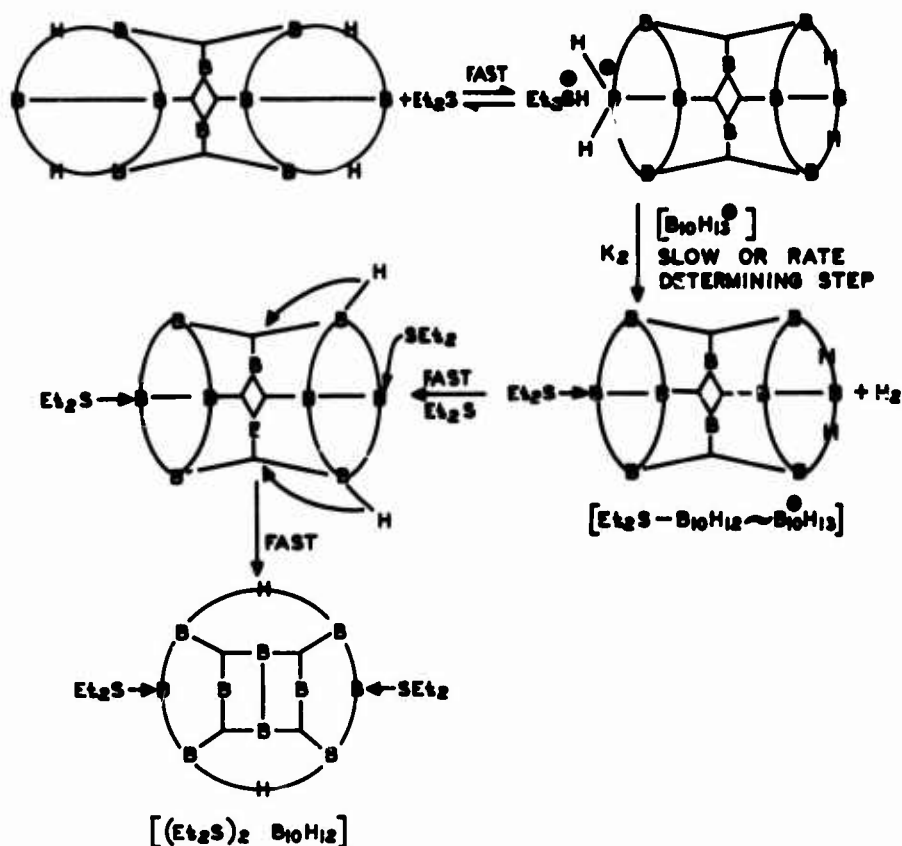
From all of the above data, the following conclusions were drawn about the reaction between ethyl sulfide and decaborane.

1. $\text{Rate} = k [\text{Et}_2\text{S}] [\text{B}_{10}\text{H}_{14}]$
2. Equilibration of B-H and B-D from bridge to terminal positions is faster than the rate at which hydrogen gas is produced.
3. A rather large deuterium isotope effect is observed which means that B-H bond breaking occurs in the rate determining step.

These facts, along with the evidence of the reaction,



(vide infra) lead to the following proposed mechanism:



The first step is a fast equilibration between decaborane and the $B_{10}H_{13}$ anion. This accounts for the fast equilibration of bridge and terminal positions. It was also noticed that in plotting the rate data an induction period was always present. This is believed to be caused by a build-up of the intermediate, $B_{10}H_{13}^{\ominus}$, to a steady state concentration. This induction period was greatest at low ethyl sulfide concentrations and when deuterated decaborane was used.

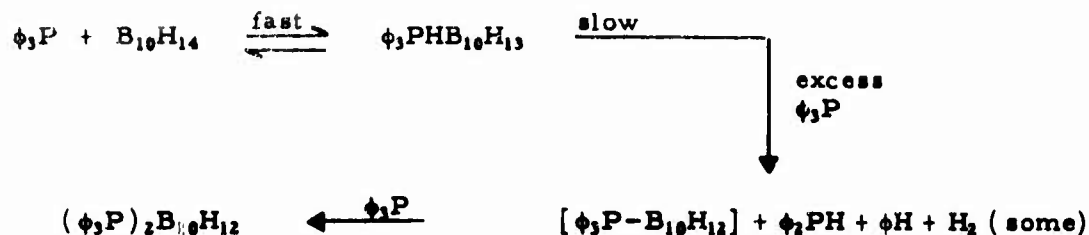
The rate determining step is shown as a four-centered collapse of the ion pair to give off hydrogen. The intermediate, $Et_2S-B_{10}H_{12}$, may have a short lifetime but is very reactive and immediately goes to product when it encounters another ethyl sulfide molecule. The formation of other $B_{10}H_{12}X_2$ molecules could well proceed by the same mechanism. Variations in the mechanism would be caused by differences in the basicity of the ligand and by the acidity of the cation in the ion pair.

B. Reactions of Phosphines with Decaborane

Some preliminary kinetic runs were made with triphenylphosphine and decaborane at 25°C. It was immediately noticed that only about one-third of the expected hydrogen was evolved and yet practically a theoretical amount of the product, $(\phi_3P)_2B_{10}H_{12}$, was isolated. As the amount of triphenylphosphine was increased, the hydrogen evolved decreased. It appeared that the phosphine was absorbing hydrogen in some way.

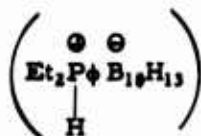
An infrared spectrum of the toluene filtrate from a run clearly showed a band at 4.2 μ which could be a P-H stretch. Also, isolation of unreacted ϕ_3P showed a strong P-H band again at 4.2 μ . None of the pure material was isolated or characterized.

The mechanism is probably similar to that proposed for ethyl sulfide except that a cleavage side-reaction may have occurred.



This would amount to the reduction of triphenylphosphine by decaborane with the elimination of benzene. When excess $B_{10}H_{14}$ was used the theoretical amount of H_2 was realized.

The reaction of $Et_2P\phi$ with decaborane was also investigated. The derivative $[Et_2P\phi]_2B_{10}H_{12}$, m. p. $162^\circ C.$, was readily formed at room temperature. During the reaction in toluene an orange intermediate complex



separated out of solution and gassed extensively. The thick insoluble complex eventually turned colorless and disappeared, whereupon gassing ceased. Again this is consistent with the general mechanism.

When $Et_2P\phi$ was reacted with bridge deuterio decaborane (see Table IV) a larger amount of deuterium was found in the evolved gas. This can be rationalized by the fact that the phosphine is much more reactive and less selective than Et_2S and hence shows less discrimination between B-H and B-D bonds.

C. New Synthesis of N-Alkyl "Dekazenes" and Unsymmetrical $B_{10}H_{12}$ Derivatives

The salt, $Et_2NH_2^+ B_{10}H_{13}^-$, prepared from diethylamine and decaborane some time ago¹, was converted to N, N, N', N'-tetraethyl dekazene when heated. The product, $(Et_2NH)_2B_{10}H_{12}$ (m. p. $202^\circ C.$),

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-57-25, Part I, Metallo-Organic Chemistry, January 1958.

was identical to the benzene soluble product prepared from bis-ethyl sulfide decaborane and diethylamine. Its infrared spectrum is shown in Fig. 12.

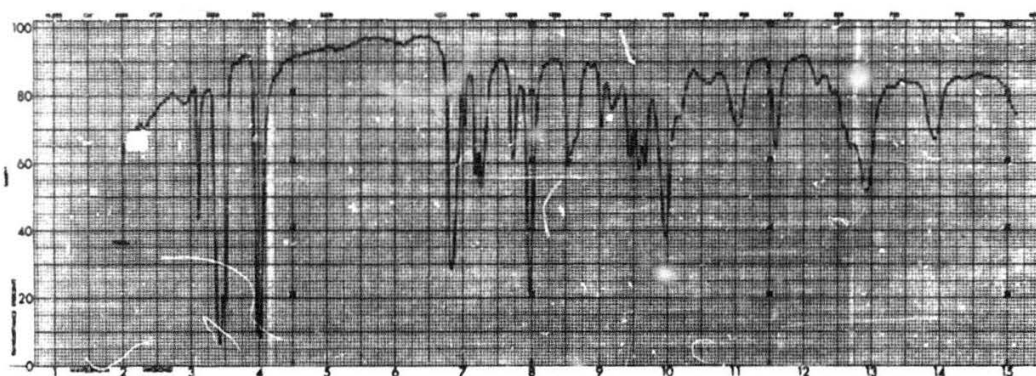
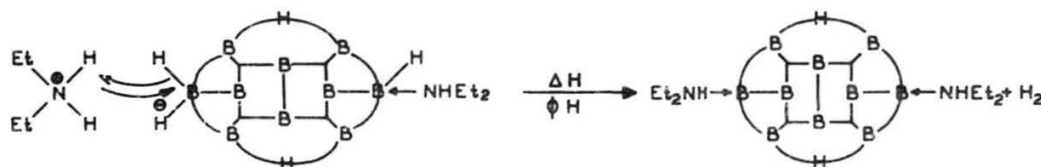
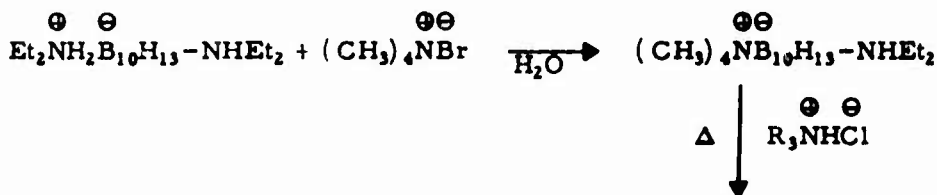


Fig. 12 Infrared spectrum of $(\text{Et}_2\text{NH})_2 \text{B}_{10}\text{H}_{12}$

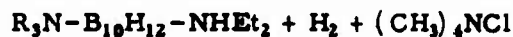
This reaction was suggested from the mechanism studies of $\text{Et}_2\text{S} + \text{B}_{10}\text{H}_{14}$ (vide supra) since both reactions involve the decomposition of similar ion pairs. Mechanistically this reaction may involve an intermediate, $\text{Et}_2\text{NH}-\text{B}_{10}\text{H}_{12}$, or merely a concerted, four-centered, collapse of the ion pair.



A simple extension of the above reaction led to a synthetic path for making unsymmetrical $B_{10}H_{12}X_2$ derivatives containing diethylamine as one ligand. This involves the preparation of the tetramethylammonium salt and subsequent decomposition in the presence of an amine hydrochloride.

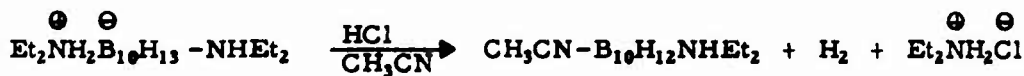


R = alkyl or hydrogen



Only a few of these unsymmetrical products have been made thus far. The compound, $Me_3N-B_{10}H_{12}-NHEt_2$, (m.p. $182^\circ C.$) was prepared in 60% yield. Other amine hydrochlorides were used but the yields were not as high. It appears that the ease of preparation is proportional to the acidity of the ammonium ions and is in the order of $3^\circ > 2^\circ \sim 1^\circ$ for the alkyl amines. As would be expected, pyridine hydrochloride reacted readily and formed the yellow derivative, $C_5H_5N-B_{10}H_{12}-NHEt_2$, m.p. $203^\circ C.$ More work is being done with this reaction.

Previously the diethylamine salt of decaborane had been treated with aqueous hydrochloric acid to yield $Et_2NH-B_{10}H_{13}$ ¹. The reaction of the salt with dry HCl in acetonitrile resulted in a mole of hydrogen and gave a product which has been fully characterized as $CH_3CN-B_{10}H_{12}-NHEt_2$.

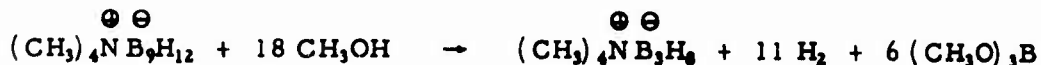


Other interesting reactions of this type are planned since many compounds of the type $X-B_{10}H_{12}-NHEt_2$ should be possible.

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, P-59-12, Part I, Metallo-Organic Chemistry August 1959.

VIII. PREPARATION OF TETRAMETHYLAMMONIUM TRIBORANE FROM TETRAMETHYLAMMONIUM NONABORANE

Tetramethylammonium triborane was formed from the slow methanolysis of $(\text{CH}_3)_4\text{N}^+\text{B}_9\text{H}_{12}^-$ ¹.



The compound, $(\text{CH}_3)_4\text{N}^+\text{B}_9\text{H}_{12}^-$, was dissolved in methanol-pentane solution and after standing for several days in the cold, small leaflets of $(\text{CH}_3)_4\text{N}^+\text{B}_3\text{H}_8^-$ (m.p. > 240°C.) appeared. The yield was only about 30%. Somewhat better results were obtained at room temperature. The salt was characterized by its analysis, B^{11} n.m.r., and infrared spectrum. An authentic sample was prepared from $\text{Na}^+\text{B}_3\text{H}_8^-$ and $(\text{CH}_3)_4\text{N}^+\text{Br}^-$ and it was identical in all respects. The infrared and B^{11} n.m.r. spectra are shown in Figs. 13 and 14.

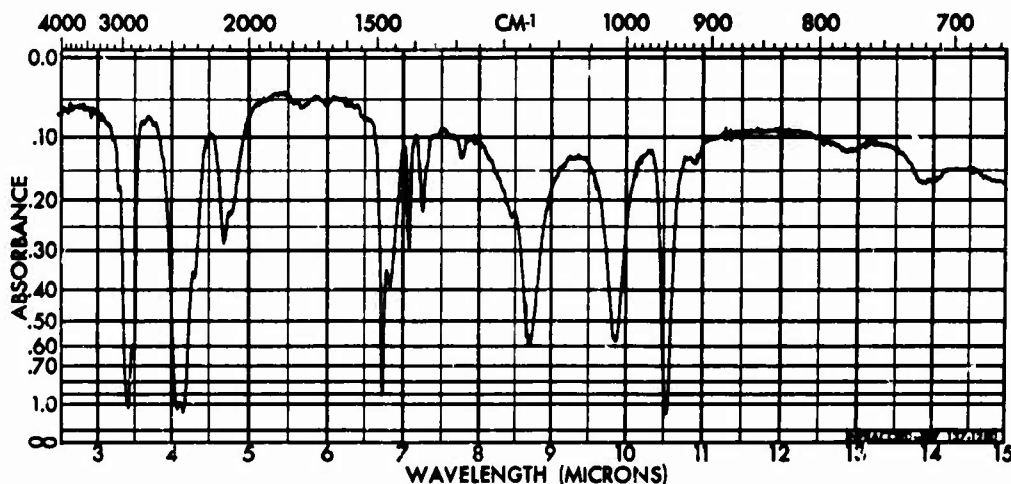


Fig. 13 Infrared spectrum of $(\text{CH}_3)_4\text{N}^+\text{B}_3\text{H}_8^-$

¹ Rohm & Haas Company, Quarterly Progress Report in Synthetic Chemistry, P-59-12, Part I, Metallo-Organic Chemistry, August 1960.

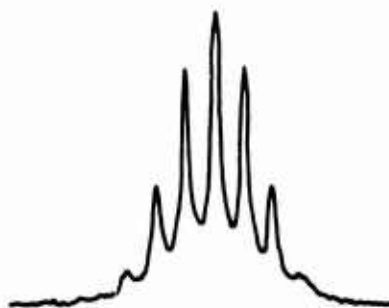


Fig. 14 B^{11} n.m.r. spectrum of $(CH_3)_4 N^+ B_3 H_8^-$

The B^{11} n.m.r. spectrum was especially enlightening. It appears to be only a septet of peaks but a careful measurement of peak heights revealed that there must be nine peaks. The peak heights were in exact agreement with the theoretical ratios for nine peaks (1:8:28:56:70:56:28:8:1) but not for seven. Phillips¹ reported the B^{11} n.m.r. for $Na^+ B_3 H_8^-$ as a septet of peaks but commented that Lipscomb had predicted nine peaks with the smallest peaks too small to observe. This was exactly what was observed and it has some theoretical significance concerning the structure of the $B_3 H_8^-$ anion. The J value of 32 cps and the center peak being +47.5 relative to methyl borate were essentially the same as reported by Phillips.

¹ W. D. Phillips, et. al., J. Am. Chem. Soc., 81, 4496 (1959)

EXPERIMENTAL

I. OCTADECABORANE-22

A. Preparation of Octadecaborane-22

Octadecaborane - A 109-g. sample of $(\text{Et}_3\text{NHB}_{10}\text{H}_{18})_n$ was dissolved in 500 ml. of 95% ethanol. The sample was passed through a large column containing ethanol saturated IR-120 in 100-ml. portions. The column was flushed clean with ethanol and reconditioned with 6 N HCl and 95% ethanol between each exchange. The eluants were evaporated to a low volume and combined. They were then retained under vacuum until only a yellow semi-solid remained. This was dissolved in 500 ml. of ether and 250 ml. of water was added with stirring over a 2.5 hour span. After addition was complete, the solution was stirred for an additional hour. A total of 1.33 liters of gas were evolved. The ether and water layers were separated and the water layer washed with four 200-300 ml. portions of ether. The ether extracts were combined and evaporated, yielding 37.8 g. of a yellow-white crystalline solid. Yield: 70.2% based on $(\text{Et}_3\text{NHB}_{10}\text{H}_{18})_n$.

Preparation of $(\text{KB}_{10}\text{H}_{18})_n$ - This salt was prepared by adding aqueous potassium hydroxide to a water suspension of $(\text{Et}_3\text{NHB}_{10}\text{H}_{18})_n$. Base was added until triethylamine was no longer evolved. The solution was then concentrated and the isolated solid was recrystallized from water-ethanol.

Preparation of $[(\text{CH}_3)_4\text{N}_{10}\text{H}_{18}]_n$ - This salt was prepared from both acid ion-exchanged and unexchanged $(\text{Et}_3\text{NHB}_{10}\text{H}_{18})_n$. The solid was dissolved in ethanol and a portion passed through IR-120. Aqueous tetramethylammonium chloride was added to each portion, producing a yellow flocculent precipitate. This was isolated and recrystallized from acetonitrile and ethanol. Infrared analysis showed the precipitates to be identical.

¹ Rohm & Haas Company. Quarterly Progress Report on Synthetic Chemistry, Part I, Metallo-Organic Chemistry, P-60-6, July 1960.

C. The Reaction of $(\text{Et}_3\text{NH})_2\text{B}_{10}\text{H}_{10}$ with Ferric Ion, another Triethylammonium Salt

Preparation of $(\text{Et}_3\text{NHB}_{10}\text{H}_{10})_n$. - A 100-g. sample of recrystallized triethylammonium perhydrodecaborate was dissolved in 500 ml. of distilled water. To this was added a solution of 150 g. of sublimed ferric chloride in 500 ml. of distilled water. The mixed solution was heated on a steam bath for 2.5 hours. The resulting suspension was cooled and the solid separated by vacuum filtration. The isolated solid was slurried in 95% ethanol and filtered. A usual, $(\text{Et}_3\text{NHB}_{10}\text{H}_{10})_n$ was isolated from the ethanol filtrate. Remaining behind in the filter was 26 g. of ethanol insoluble material, yield: 42% based on the composition $(\text{Et}_3\text{NHB}_{10}\text{H}_{10})_n$. This was recrystallized from ethanol, but only a small quantity of solid dissolved in ethanol, even at the boiling point. The solid melted with decomposition at $202-203^\circ$.

Anal. Calc'd for $\text{C}_6\text{H}_{24}\text{B}_{10}\text{N}$: C, 36.63; H, 12.21; B, 44.04; N, 7.1.

Found: C, 37.04; H, 12.06; B, 43.59; N, 7.79.

II. DICA' BOUNDECABORANE-13 CHEMISTRY

A. Resolution of a Nonacarborane

11-Methyl-12-Phenylcarborane. - A solution of 25 g. (0.40 mole) of butyllithium in 400 ml. of pentane was added slowly to 75 g. (0.34 mole) of phenylcarborane dissolved in 100 ml. of ether. The reaction mixture was stirred and cooled to 0° during the addition. The yellowish solution was then warmed to room temperature to evaporate most of the butane produced. Eighty five grams (0.6 mole) of methyl iodide was added after cooling to 0° and the solution was allowed to warm to room temperature, again while being stirred overnight. The mixture was poured onto 450 ml. of crushed ice containing 45 ml. of concentrated H_2SO_4 . An orange ether layer was obtained which was separated and the aqueous layer was extracted twice with 200 ml. of ether. The combined

other extracts yielded, after drying over magnesium sulfate, 73 g. of yellowish crystals, which were chromatographed on basic alumina in pentane. An 88% yield (70 g.) of pure 11-methyl-12-phenylcarborane was obtained, m.p. 100.5-101°.

Resolution of 11-methyl-12 phenylnonacarborane-brucine. -

11-Methyl-12-phenylcarborane (70 g., 0.30 mole) was degraded by heating it in 150 ml. of 30% methanolic potassium hydroxide to 50-60° until a small sample of solution was completely water soluble. The clear solution was neutralized carefully with hydrogen chloride gas while cooling in ice water. Precipitated potassium chloride was filtered off and the solvent was evaporated in vacuum. The residue was dissolved in 200 ml. of water and added to an aqueous solution of 150 g. of brucine. 11-Methyl-12-phenylnonacarborane-brucine precipitated instantaneously. A 185 g. yield of crude product was obtained.

Anal. Calc'd for $B_9C_{12}H_{15}N_2O_4$: C, 62.07; H, 7.32.

Found : C, 62.47; H, 7.38.

Resolution of the diastereomers was achieved by dissolving the crude salt in approximately 1500 ml. hot acetonitrile. When the filtered solution was allowed to cool slowly to room temperature, slightly yellowish crystals precipitated which were filtered off in 20-30 g. fractions. The mother liquor was successively concentrated until 85% of the product was recovered. The fractionation was repeated four times and fractions of approximately equal optical activity combined. Top fractions yielded 25 g. of salt with a molar rotation of $\alpha_{\text{mol.}} = -17.4^\circ$. End fractions (14 g.) possessed a molar rotation of $+13.0^\circ$. Optical activity was checked by measuring approximately 0.5 M solutions in dimethylformamide.

Conversion to the Free Nonacarborane. -

Twenty-five grams of 11-methyl-12-phenylnonacarborane-brucine ($\alpha_{\text{molar}} = 17.4^\circ$) was heated in 100 ml. of 30% ethanolic potassium hydroxide for 30 minutes. During that time the solution turned brown and became water soluble. Dilution with 200 ml. of water and addition of excess aqueous tetramethylammonium chloride precipitated the corresponding salt which was recrystallized from methanol. After two crystallizations 8.9 g. of white

crystals was obtained. Molar rotation was -16.8° . Three grams of the pure salt was dissolved in 40 ml. of methanol and run through the acid form of amberlite IR 120. Evaporation of the solvent left a colorless oil which crystallized within two days while drying in the vacuum line. A 2.1 g. yield of pure 11-methyl-12-phenylnonacborane was obtained. The molar rotation was found to be -14.8° .

B. Kinetics of the Formation of Nonacborane

m- and p-Nitrophenylcarborane. - A 100 g. sample (0.45 mole) of phenylcarborane was nitrated as described in Rohm & Haas Company Quarterly Progress Report, P-58-12, Part I. All operations were carried out remotely. A total of 87 g. (73%) of m and p-nitrophenylcarborane was obtained. The isomers were separated by fractional crystallization. The less soluble compound was obtained from carbon tetrachloride and melted at $167-168^{\circ}$. The mother liquor was stripped and the residue crystallized several times from cyclohexane. An 18 g. yield of slightly yellowish needles melting at $120-122^{\circ}$ was obtained.

Identification of m- and p-Nitrophenylcarborane. - In order to show the identity of the isomers, 3 g. of the less soluble, high melting compound (m.p., 167°) was degraded in 10 ml. 20% ethanolic potassium hydroxide. The dark brown solution was acidified with concentrated sulfuric acid and potassium permanganate added until a pink color remained. During this procedure the mixture was stirred and heated to $60-80^{\circ}$. The resulting suspension was neutralized with 10% sodium hydroxide and filtered while warm. Acidification and concentration of the filtrate produced nearly white crystals which melted at 241° . The infrared spectrum was identical with that of p-nitrobenzoic acid.

Aminophenylcarborane. - Five grams (0.018 mole) of p-nitrophenylcarborane was dissolved in 80 ml. of warm glacial acetic acid and added to a vigorously stirred suspension of 8 g. of iron powder in 60 ml. of glacial acetic acid. When the mixture was heated carefully, the reaction took place at $60-65^{\circ}$ and caused a sudden temperature rise to

110°. After cooling, the temperature was maintained at 60-70° for two hours and the slurry was poured into 500 ml. of cool water. The amine was extracted twice with 200 ml. portions of ether. Washing with 3% sodium carbonate removed acetic acid. After drying over magnesium sulfate, removal of the solvent left a brownish oil which crystallized while drying on the vacuum line. Recrystallization from methanol-water produced a 94% yield of white, feathery crystals, m.p. 104-105°.

Analogous treatment of m-nitrophenylcarborane (m.p. 120-122°) led to m-aminophenylcarborane (m.p. 63°) in about the same yield. The compound resisted all attempts at crystallization but solidified after 5 days without solvent while under vacuum.

III. CARBORANE CHEMISTRY

A. Electrophilic Exchange of Deuterium Chloride with Carborane

The apparatus and techniques previously described¹ were employed. As in the DCl/B₁₀H₁₄ exchange studies, 8.64 g. (0.06 moles) of carborane and 6.0 g. (0.045 mole) of anhydrous aluminum chloride in 60 ml. of carbon disulfide were stirred for 14 hours at 27°C ± 0.05°C. in a stream of deuterium chloride at a flow rate of approximately 3.9-4.0 liters/hour. Samples were withdrawn every hour, filtered under dry nitrogen, and the B¹¹ n.m.r. spectra recorded using a Varian High Resolution Spectrometer operating at 12.8 mc. The product was recovered by filtering off the aluminum chloride in vacuum and evaporating the carbon disulfide from the resulting filtrate. The slightly brown, solid residue was dissolved in pentane and passed through a column of neutral alumina. Removal of the pentane produced the pure deuterated material. No change in the infrared spectra was observed as a result of the alumina

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, Part I, Metallo-Organic Chemistry, No. P-60-6, July 1960.

treatment.

1,2,3,4-deuterium labeled carborane. - Into a dry 3-l. stainless steel Hoke cylinder was placed 20.0 g. of anhydrous aluminum chloride, 24.4 g. (0.2 mole) of decaborane and 350 ml. of dry carbon disulfide. The tank was cooled to -196° and evacuated. Approximately four moles of deuterium chloride (containing approximately 2% HCl) was condensed into the cylinder, which was then closed off and allowed to warm to room temperature. After shaking for approximately eighteen hours the deuterium chloride was bled off and the reaction solution filtered under dry nitrogen. The carbon disulfide was removed and the resulting solid was sublimed. There was isolated 23.5 g. of the deuterated decaborane which upon analysis gave a mole D/mole of $B_{10}H_{14}$ value of 3.7. The B^{11} n.m.r. spectrum of this material was consistent with 1,2,3 and 4 substitution. The decaborane was converted to the bis-acetonitrile derivative in approximately 95% yield by simply refluxing an acetonitrile solution of the hydride for four hours.

The reaction of the deuterated BAND with acetylene using acetonitrile solvent was carried out in a 300-cc. stainless steel autoclave equipped with a stirrer, at $80^{\circ}C$. for five hours. The yield of the pure deuterated carborane was twenty to twenty-five percent based on BAND.

IV. REACTIONS OF $RBH_2 \cdot N(CH_3)_3$ WITH HYDRAZINE

Pyrolysis of hydrazine t-butylborane. - A 6.8-g. sample of hydrazine t-butylborane was placed in a 100-cc. round-bottomed flask equipped with a condenser and drying tube. The flask was immersed in an oil bath and the bath was heated to 150° and kept at this temperature for three hours. Gas was evolved during the reaction. The mixture was cooled, dissolved in ether, and extracted with water. Separation, drying, and evaporation of the ether left 4.8 g. of a white solid which could be recrystallized from ether-low boiling petroleum ether as white needles, m.p. $161-162^{\circ}$.

Anal. Calc'd for $[B_4H_{11}BN_2]_x$: C, 49.04; H, 11.32; N, 28.60; B, 11.04.
Found : C, 49.08; H, 11.60; N, 28.67; B, 10.90.

Deuteration of pyrolysis product. - One-half gram of the white solid, m.p. 161-162°, was dissolved in 20 cc. of absolute ether and 5 cc. of deuterium oxide was added. The mixture was allowed to stir at room temperature for twenty minutes and the layers were then separated. After drying the ether layer over magnesium sulfate, it was evaporated leaving 0.46 g. of a white solid which showed N-D absorption and N-H absorptions in the infrared. Repetition of this reaction with the product obtained did not give a product which contained more deuterium.

Iodine reaction with pyrolysis product. - To a solution of one gram of the pyrolysis product in 20 cc. of ether was added in dropwise fashion an ethereal solution of two grams of iodine. The first few drops of the iodine solution were decolorized and then the mixture began to turn dark and a precipitate formed. The reaction mixture was allowed to stir overnight and was then filtered. A red-black solid, 1.35 g., was collected. This solid and the filtrate were then added to a 10% sodium thiosulfate solution and 200 cc. of ether was added; the color was removed and a light yellow solid, which was insoluble in both the ether and aqueous layers, was collected on a filter. This material, 0.48 g., m.p. 132-133°, was treated with ethanol and the color was removed although the material did not dissolve. The white product thus obtained melted at 134-135° but the infrared spectrum was different from that of the 132-133° material. Analysis is in progress. Evaporation of the ether layer provided at least two products which have not been investigated.

Acetylation of pyrolysis product. - A solution of one gram of the pyrolysis product in twenty milliliters of acetic anhydride was prepared by heating the mixture on the steam bath. When all of the solid had dissolved, four drops of concentrated sulfuric acid were added and the mixture was heated on the steam bath for ten minutes, during which time a yellow color developed. The mixture was poured into 800 cc. of water and this was stirred until the oily material which separated became solid. The white solid product, 0.9 g. was collected

on a filter and washed with water. Recrystallization from ether-low boiling petroleum ether provided white crystals, m.p. 140-141°. Recrystallization could also be effected from carbon disulfide.

Anal. Calc'd for $B_9H_{13}BN_2O_2$: C, 52.78; H, 8.31; N, 15.39; B, 5.94.
Found: C, 51.42; H, 8.24; N, 8.51; B, 6.23.

Found: C, 52.82; H, 8.19; N, 9.16; B, 6.40.
Calc'd for $C_8H_{13}BNO_3$: C, 52.21; H, 8.22; N, 7.61; B, 5.88.

Infrared analysis shows that the material is unstable in the air; an -OH band appears in the spectra of samples which are kept for a few days. This band can be removed by washing the product with water.

VI. AROMATIC ORGANOBORANES

o-Diethynylbenzene. - A solution of potassium t-butoxide was prepared by addition of 1.25 g. (0.0316 g. atom) of potassium to 50 cc. of t-butyl alcohol. The solution was heated to the boiling point and 3.4 g. (4.55×10^{-3} mole) of o-bis(1,2-dibromoethy)benzene dissolved in 20 cc. of t-butyl alcohol was added dropwise. After heating the mixture at the reflux temperature for one hour, it was cooled and poured into water. Extraction with ether and drying of the extracts, followed by removal of the solvent, gave a brown liquid which was distilled in vacuum to provide 0.33 g. of a clear liquid, b.p. 80-85°/13 mm., whose infrared spectrum indicated it to be o-diethynylbenzene. Some o- α -bromovinylethynylbenzene was also isolated.

VII. REACTIONS OF DECABORANE

A. The Kinetics and Mechanism of $B_{10}H_{12}(Et_2S)_2$ Formation

Materials. - The decaborane was sublimed before use. Ethylsulfide (Eastman, white label) was distilled from CaH_2 on a spinning band column.

The toluene was distilled from LiAlH_4 and only the middle portion was collected.

Rate Run Procedure. - The apparatus consisted of a Warburg Manometer, calibrated to 0.1 cm., and a reaction flask which was completely immersed in the constant temperature bath. A drawing of the reaction vessel is shown in Fig. 15.

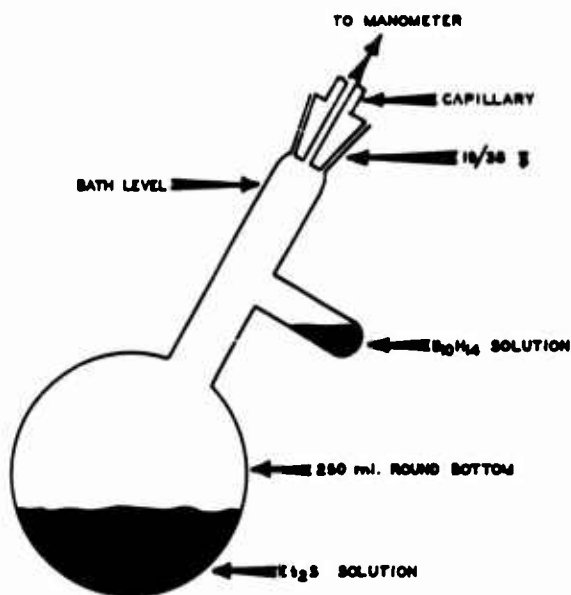


Fig. 15 Reaction vessel used for rate runs.

Five milliliters of the decaborane solution of known concentration was placed in the small side arm and the ethyl sulfide solution (previously diluted to the mark in a 50 ml. volumetric flask at the bath temperature) was placed in the bottom of the flask along with some boiling chips. The solutions were allowed to equilibrate until no more pressure was observed on the manometer.

The flask was then rotated in such a fashion as to allow the decaborane solution to drain into the reaction zone. Pressure readings

were recorded at various time intervals. The infinity pressure was calculated from the gas law equation and was also checked experimentally in some cases. A typical plot of $\log P$ vs. time is shown in Fig. 16. Since the reaction was run under pseudo first order conditions the rate constant was calculated from the following equation:

$$K_2 = \frac{(\text{slope}) (-2.303)}{(Et_2S)}$$

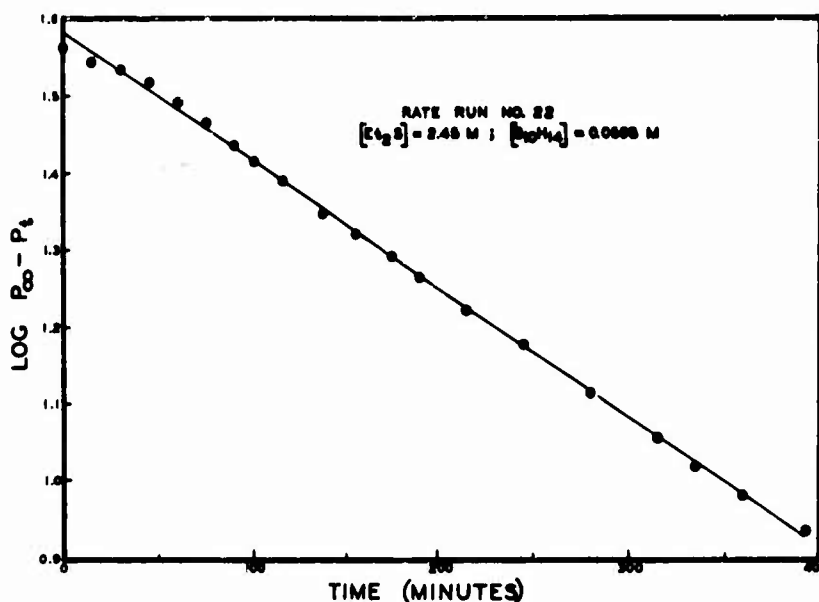


Fig. 16 Typical plot of rate run.

C. New Synthesis of N-alkyl "Dekazenes" and Unsymmetrical $B_{10}H_{12}$ Derivatives

Preparation of $Et_2NH_2^+ - B_{10}H_{11}^- - NHEt_2$. - This reaction consisted of merely adding a solution of 2 g. of $B_{10}H_{14}$ in 25 ml. of ether to a cold solution of 17 ml. diethylamine in 25 ml. of ether and allowing the mixture to stand for several hours. The yellow gummy mass which formed initially

gradually changed to a white solid. Four grams of crystalline product was obtained after recrystallization from water, decomposition point, 203-204°C. This compound was previously characterized.¹

⑨ Preparation of $(Et_2NH)_2B_{10}H_{12}$. - A solution of 1 g. of the salt, $Et_2NH_2B_{10}H_{13}-NH_4Et_2$ in 20 ml. of benzene was refluxed with stirring under nitrogen for two hours. Hydrogen gas was evolved. The benzene solvent was then stripped off and the solid residue was recrystallized from methylene chloride-pentane. The yield of product was 0.8 g., decomposition point, 202-203°C. The infrared spectrum of this compound was identical to that of the benzene soluble isomer obtained from the reaction of diethylamine and bis-ethyl sulfide decaborane; the compound was characterized as $(Et_2NH)_2B_{10}H_{12}$.

⑩ Preparation of $(CH_3)_4NB_{10}H_{13}-NH_4Et_2$. - To a solution of 4 g. of $Et_2NH_2B_{10}H_{13}-NH_4Et_2$ in hot water was added 6 g. of tetramethylammonium bromide. After cooling and filtering, 4 g. of crystals were isolated. The compound did not melt up to 260°C.

Anal. Calc'd for $B_{10}C_4H_{26}N_2$: B, 40.34; C, 35.79; H, 13.42; N, 10.44.
Found: B, 40.81; C, 34.69; H, 13.58; N, 10.27.

⑪ Preparation of $(CH_3)_3N-B_{10}H_{12}-NH(C_2H_5)_2$. - A solution of 1 g. $(CH_3)_4NB_{10}H_{13}-NH_4Et_2$ and 0.5 g. $(CH_3)_3NHCl$ in 20 ml. benzene was refluxed for two hours or until no more H_2 was evolved. The insoluble material was filtered off and the benzene was evaporated from the filtrate. Recrystallization of the solid residue from methylene chloride-pentane gave 0.7 g. of product which melted at 182-183°C.

Anal. Calc'd for $B_{10}C_7H_{32}N_2$: B, 42.90; C, 33.31; H, 12.69; N, 11.10.
Found: B, 43.06; C, 33.38; H, 12.89; N, 10.74.

Preparation of $C_5H_5N-B_{10}H_{12}-NH_4Et_2$. - The procedure was the same as above. A solution of 1 g. of $(CH_3)_4NB_{10}H_{13}-NH_4Et_2$ and 0.7 g. of pyridine hydrochloride in 20 ml. of benzene was refluxed for two hours

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry Part I, Metallo-Organic Chemistry, No. P-57-25, January 1958.

Work-up of the solutions gave 0.8 g. of yellow product, m.p. 204°C .

Yellow needles were obtained from methylene chloride-pentane.

Anal. Calc'd for $\text{B}_{10}\text{C}_7\text{H}_{28}\text{N}_2$: B, 39.75; C, 39.68; H, 10.29; N, 10.29.

Found : B, 39.00; C, 41.61; H, 11.23; N, 11.07.

VIII. PREPARATION OF TETRAMETHYLAMMONIUM TRIBORANE FROM TETRAMETHYLAMMONIUM NONABORANE

Tetramethylammonium Triborane. - Ten grams of $\text{Me}_4\text{NB}_9\text{H}_{12}$ ¹ was dissolved in about 300 ml. of methanol at room temperature and pentane was added until the solution turned cloudy. The mixture was placed in a refrigerator for about five days. Slow gassing occurred and leaflets finally separated out. The material (2.3 g.) was collected in a filter and recrystallized from methanol as feathery leaflets, m.p. $>240^{\circ}\text{C}$.

Anal. Calc'd for $\text{B}_3\text{C}_4\text{H}_{20}\text{N}$: B, 28.36; C, 41.94; H, 17.47; N, 12.23.

Found : B, 28.45; C, 39.89; H, 17.27; N, 11.92.

¹ Rohm & Haas Company, Quarterly Progress Report on Synthetic Chemistry, Part I, Metallo-Organic Chemistry, No. P-59-12, August 1959.

**Initial distribution of this report was made
in accordance with the Joint Army-Navy-
Air Force mailing lists for Solid Propellant
and Liquid Propellant technical information
plus approved supplements**